

STUDIES OF POLY-YNE POLYMERS CONTAINING TRANSITION METALS IN THE MAIN CHAIN

III *. SYNTHESIS AND CHARACTERIZATION OF A POLY-YNE POLYMER CONTAINING MIXED METALS IN THE MAIN CHAIN, $\text{--[trans,trans-Pt(PBu}_3)_2\text{--C}\equiv\text{C--C}\equiv\text{C--Pd(PBu}_3)_2\text{--C}\equiv\text{C--C}\equiv\text{C--}]_{n/2}$ **

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(Received June 12th, 1978)

Summary

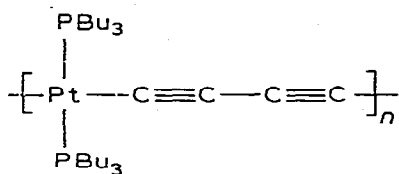
By the reaction of *trans*-(PBu₃)₂Pt(C≡C–C≡CH)₂ with *trans*-(PBu₃)₂PdCl₂, the title polymer, $\text{--[trans,trans-Pt(PBu}_3)_2\text{--C}\equiv\text{C--C}\equiv\text{C--Pd(PBu}_3)_2\text{--C}\equiv\text{C--C}\equiv\text{C--}]_{n/2}$ (II), has been prepared and characterized by spectral and analytical data. The alternating regularity of the metal arrangement in II was confirmed by the selective formation of the trinuclear complex *trans,trans,trans*-ClPd(PBu₃)₂–C≡C–C≡C–Pt(PBu₃)₂–C≡C–C≡C–Pd(PBu₃)₂ (III), in the depolymerization by *trans*-(PBu₃)₂PdCl₂ using CuI as catalyst in NEt₂.

Introduction

A wide range of polymers containing metallocene derivatives [1] or transition metal carbonyl derivatives [2] have been reported. These polymers are of interest because of their potential catalytic activity and physical properties. In previous papers [3,4] we reported the Pt–poly-yne polymer I having a backbone composed of conjugated poly-ynes and platinum atoms as the first example of polymers containing σ -bonded transition metal atoms in the main chain. Polymer I (M_w 120 000) is easily soluble in aprotic organic solvents as methylene chloride, diethylamine, benzene, toluene, THF and even in n-hexane. The high solubility of I is thought to be attributed to the butyl substituents at phosphorus. From various evidence based on the ³¹P NMR and behaviour in solution, it was

* For part II see ref. 4.

** Dedicated to Professor Ernst Otto Fischer on the occasion of his 60th birthday on November 10, 1978.



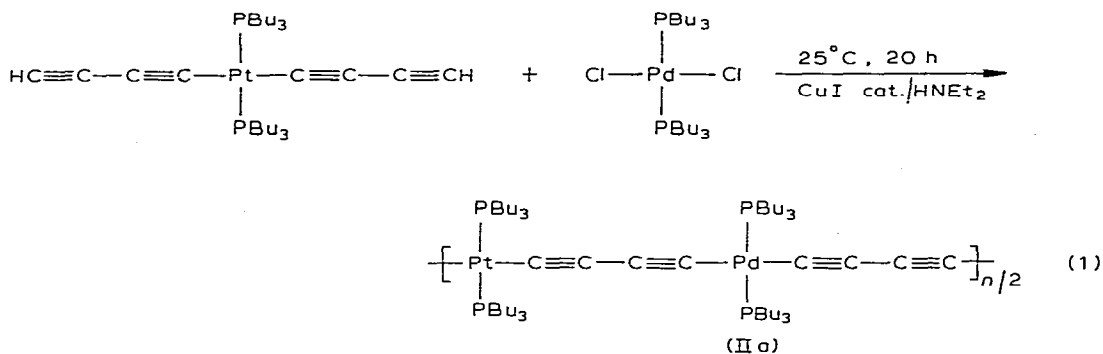
(I)

concluded that the polymer has the all-*trans* configuration at the platinum moiety and a rigid rod-like structure in solution [4].

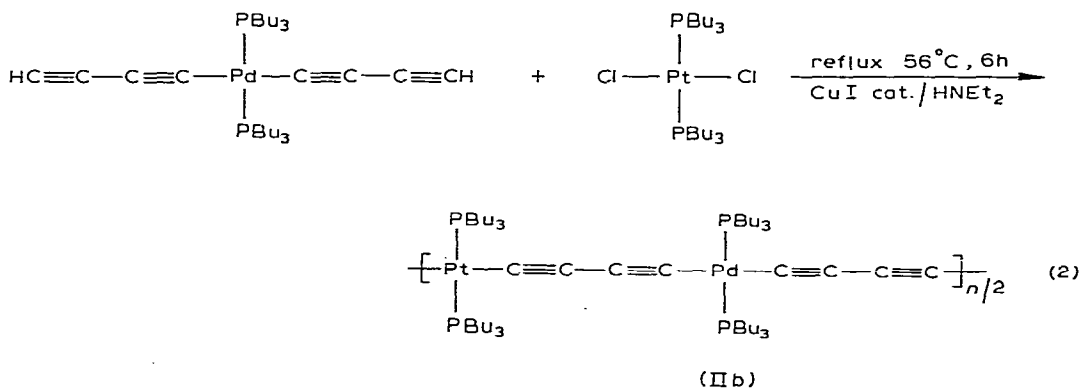
In connection with the studies of such polymers, we have investigated poly-yne polymers containing alternate arrangements of platinum and palladium atoms in the backbone. We hope that such polymers, in which different kinds of metals are regularly arranged at appropriate distances, will serve as special models for studying physical properties and catalytic activity. The synthesis and characterization of Pt-Pd mixed polymers are described below.

Results and discussion

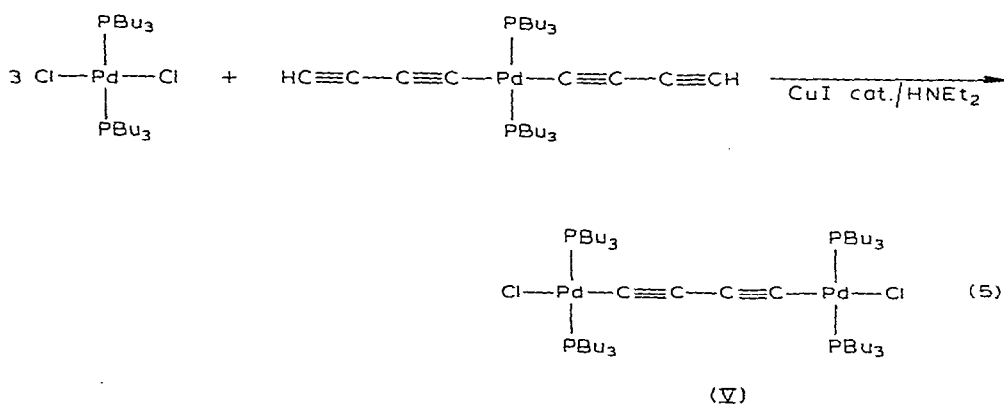
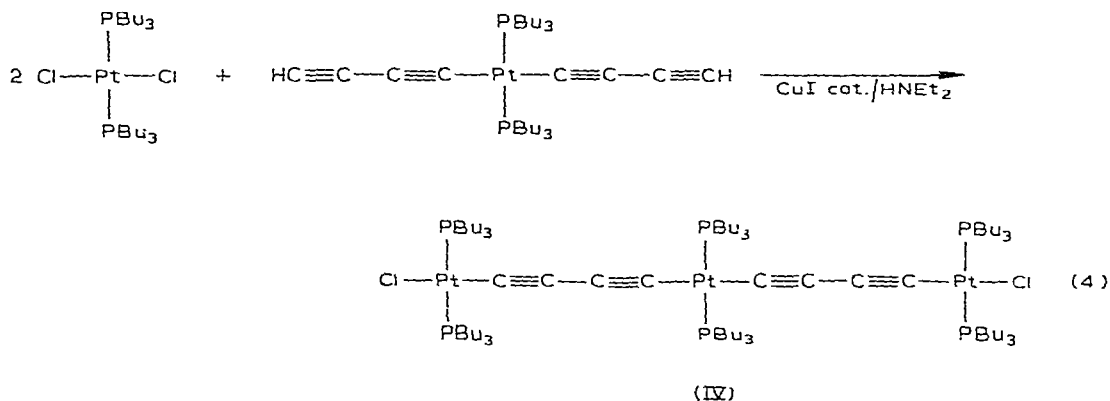
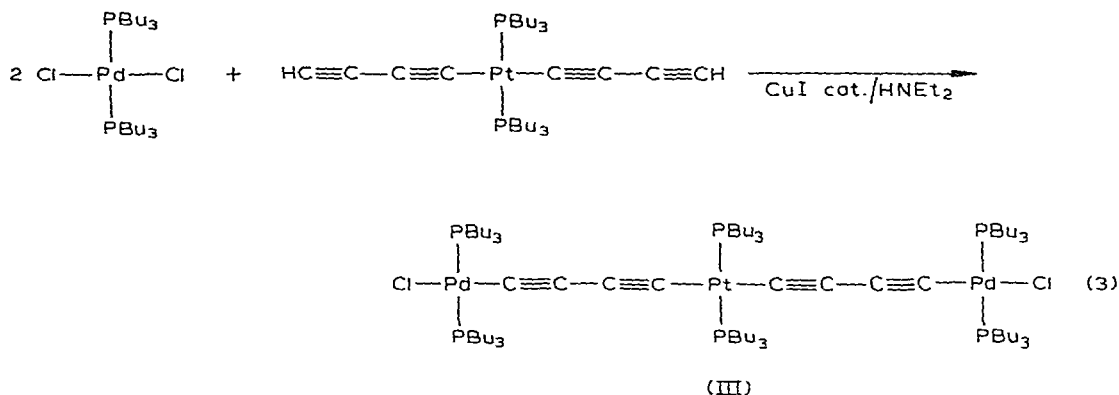
Polymers containing alternate platinum and palladium atoms in the backbone are prepared by the following two methods: (i) reaction of *trans*-(PBu₃)₂Pt-(C≡C-C≡CH)₂ with *trans*-(PBu₃)₂PdCl₂ (eq. 1), (ii) reaction of *trans*-(PBu₃)₂Pd-



(C≡C-C≡CH)₂ with *trans*-(PBu₃)₂PtCl₂ (eq. 2). Both reactions gave air-stable, pale-yellow polymers, IIa and IIb.



In order to obtain structural information on the mixed metal polymers, three model complexes, III, IV and V, were prepared by the following reactions (eq. 3, 4, 5). The formation of the Pd-dinuclear complex V in eq. 5, could indicate



that dehydrochlorination [5] and symmetrization (vide infra) take place simultaneously.

Tables 1 and 2 list some physical properties, characteristic spectral data and analytical data of polymers IIa, IIb and related model complexes. The ^{31}P NMR spectrum (Fig. 1) and ESCA data of IIa are consistent with a 1/1 ratio of platinum to palladium, an all *trans*-configuration [3] of platinum and palladium, and

TABLE I
PHYSICAL PROPERTIES OF COMPOUNDS II-VI

Compound	Color	M.p. (°C) or dec. (°C) ^a (under N ₂)	$\nu(\text{C}\equiv\text{C})$ ^b (cm ⁻¹)	Analysis found (calcd.) (%)				Mol. wt. ^c (calcd.) or \bar{M}_w ^d
				C	H	P	Cl	
IIa	Pale yellow	194 (dec.) (251)	1985m 2110w	55.2 (55.7)	8.9 (9.0)	9.5 (10.3)	26 000	
IIb	Pale yellow	173 (dec.) (207)	1985m 2110w	55.0 (55.7)	8.7 (9.0)	9.4 (10.3)	7000	
III	Yellow	65.0-66.0	1992m 2290w	54.1 (54.7)	9.8 (9.5)	11.1 (10.9)	1711 (1788)	
IV	Yellow	66.0-66.5	1990m 2280w	48.7 (48.9)	8.5 (8.3)	8.9 (9.4)	1814 (1966)	
V	White	102.0-102.5	2000m 2280w	54.1 (54.7)	9.8 (9.5)	11.1 (10.9)	1114 (1141)	
VI	Pale yellow	153 (dec.) (196)	1978m 2240w	59.8 (59.5)	9.9 (10.3)	11.1 (11.0)	35 000	

^a From thermal gravimetric analysis in air. ^b In Nujol. ^c VPO in CH₂Cl₂. ^d Measured by GPC [4] using α and K values of 1.7 and 6.5×10^{-9} , respectively.

with Pt^{II} and Pd^{II}-oxidation states in the polymer backbone. IIa and IIb are essentially indistinguishable from one another on the basis of the spectral data mentioned above alone.

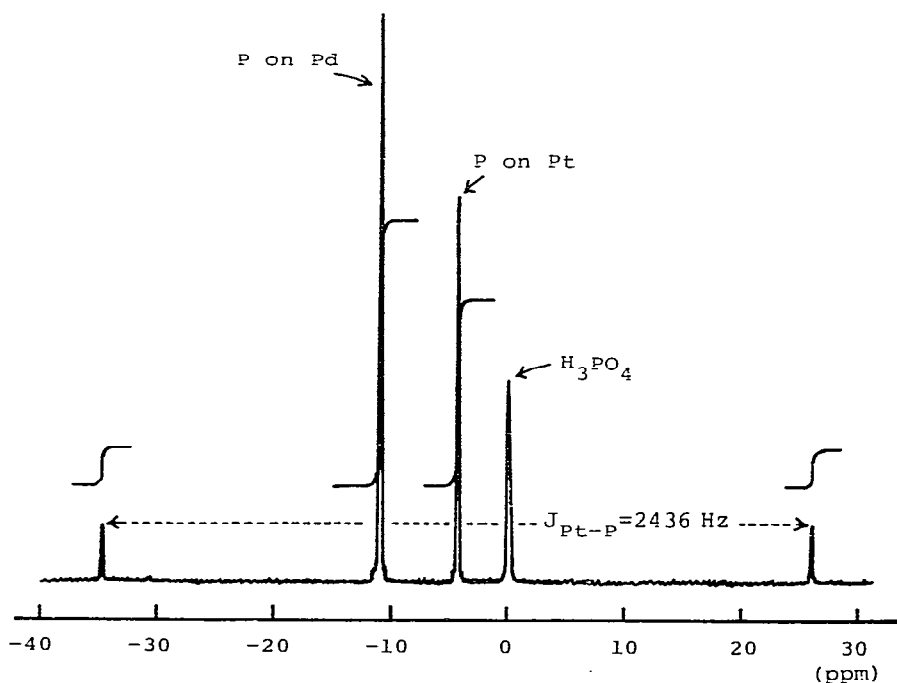


Fig. 1. ³¹P {¹H} NMR spectrum of $-\{\text{Pt}(\text{PBU}_3)_2-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{Pd}(\text{PBU}_3)_2-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\}_{n/2}$ (IIa) in CH₂Cl₂.

TABLE 2
ESCA, UV AND $^{31}\text{P}\{^1\text{H}\}$ DATA OF COMPOUNDS II-VI

Compound	ESCA (in eV) ^a		λ_{max} (nm) ($\epsilon \times 10^{-4}$) ^b		$^{31}\text{P}\{^1\text{H}\}$ spectra		$J(\text{Pt-P})$ (Hz)				
	Pt		Pd		δ ^c (ppm) PBu ₃ on	Pt					
	4f ^{7/2}	4f ^{5/2}	3d ^{5/2}	3d ^{3/2}							
IIa	72.7	76.1	338.0	343.0	265 (1.39)	286 (1.27)	340 (1.17)	364 (2.49)	-11.03	-4.38	2436
IIb	72.8	76.2	338.0	343.3	265 (1.55)	287 (1.40)	340 (1.52)	365 (1.86)	-11.03	-4.37	2437
III	72.8	76.2	338.0	343.3		281 (3.28)	343 (5.70)		-9.66	-4.17	2368
IV	72.8	76.2			269 (3.08)	289 (2.90)	336 (3.52)	360 (2.96)		-4.34	2376
V			338.0	343.0	263 (8.26)	276 (8.09)	299 (3.35)		-9.83	-7.28	2435
VI			338.1	343.1	287 (1.67)	314 (1.55)	342 (2.12)		-10.74		

^a X-ray photoelectron binding energies were measured on sticky tape and were referenced to the carbon 1s line (taken to be 285.0 eV) of each sample. ^b Measured in CH₂Cl₂. ϵ for the polymer, IIa, IIb and VI were calculated based on their monomer unit, $[\text{M}(\text{PBu}_3)_2-\text{C}=\text{C}-\text{C}=\text{C}]_n$. ^c Measured in CH₂Cl₂. ^{31}P shift in δ ppm from external H₃PO₄ (positive shifts to high field).

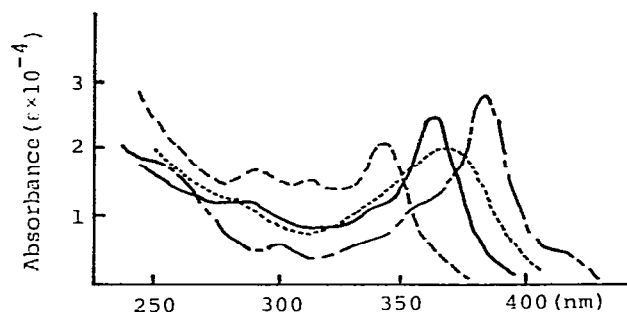
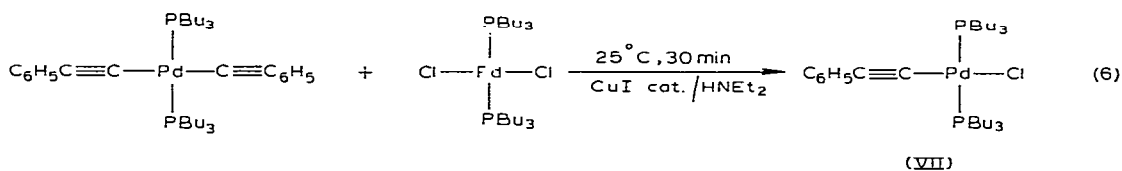


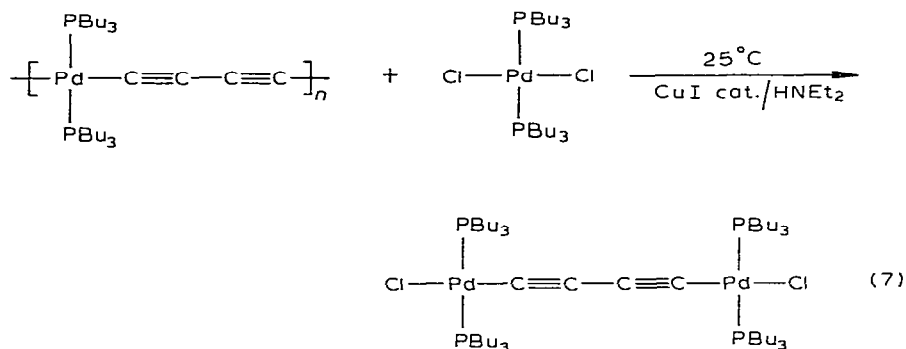
Fig. 2. Electronic spectra of the polymers in CH_2Cl_2 : ——— $\{trans,trans\text{-Pt}(\text{PBu}_3)_2\text{-C}\equiv\text{C-C}\equiv\text{C-Pd}(\text{PBu}_3)_2\text{-C}\equiv\text{C-C}\equiv\text{C}\}_n$ (IIa); - - - - $\{trans\text{-Pt}(\text{PBu}_3)_2\text{-C}\equiv\text{C-C}\equiv\text{C}\}_n$ (I); - · - · $\{trans\text{-Pd}(\text{PBu}_3)_2\text{-C}\equiv\text{C-C}\equiv\text{C}\}_n$ (VI); ······ IIb.

We have examined the electronic spectra of four polymers in CH_2Cl_2 solution (Fig. 2). Analogous to other acetylide complexes [6,7], we assign the lowest energy bands to the charge transfer bands of the metal-alkynyl bonds, which have λ_{max} values of 342, 364 and 384 nm for the Pd-Pd, Pt-Pd, and Pt-Pt polymer types, respectively. The Pt-Pd polymer IIa shows a sharp absorption band, the Pd-Pt polymer IIb a broad one. These data indicate that the alternate arrangement in IIb is somewhat disordered.

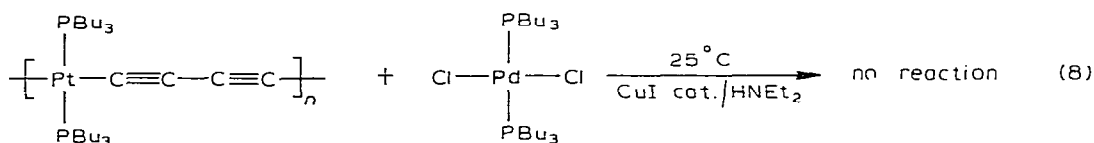
Further evidence for the regularity of the metal arrangement in IIa was obtained from the product distribution after depolymerization. In transition metal acetylide chemistry, CuI shows a wide variety of catalytic functions. First, CuI catalyzes alkynylation of the metal halide in amine [5]. In HNEt_2 and under reflux conditions, CuI catalyzes the isomerization of *cis*-dialkynylplatinum complexes to the *trans*-isomer. CuI catalyzes also the symmetrization between dialkynylmetal complexes and metal chlorides. For example, a mixture of *trans*-(PBu_3)₂Pd($\text{C}\equiv\text{CC}_6\text{H}_5$)₂ and *trans*-(PBu_3)₂PdCl₂ gave, quantitatively, *trans*-(PBu_3)₂PdCl($\text{C}\equiv\text{CC}_6\text{H}_5$) (VII) (eq. 6).



Depolymerization of the palladium-poly-yne polymer VI, by *trans*-(PBu_3)₂-PdCl₂ in HNEt_2 in the presence of CuI catalyst, gave the palladium dimer V, quantitatively. In fact, selective cleavage of the Pd-C bond, weakened by the *trans*-alkynyl group, may take place quite easily at room temperature affording V. As the stability of the metal-carbon bond increases in passing from Pd to Pt, we noticed that, in the case of the platinum polymer I, such depolymerization occurs very slowly even under reflux. In the reaction at room temperature, the starting polymer I is recovered quantitatively (eq. 8).

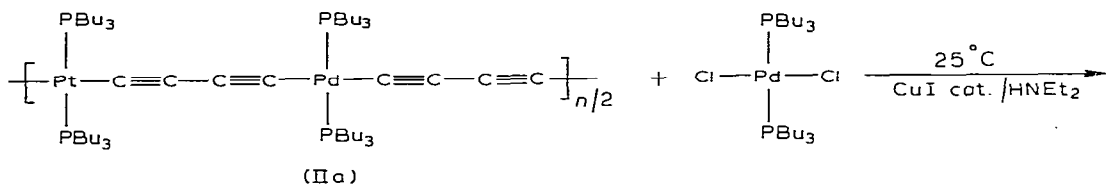


(V)

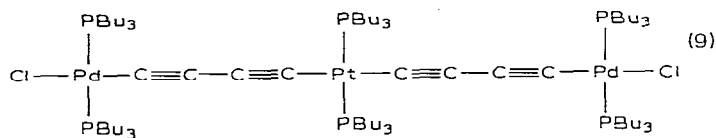


(I)

Considering the above it is tempting to conclude that the polymer IIa prepared according to eq. 1 represents a more efficient method for preparing polymers having a regularly alternate arrangement of platinum and palladium in the backbone. The alternate regularity of IIa was also confirmed by the following depolymerization with *trans*-(PBu₃)₂PdCl₂. On treatment of a mixed alternating metal polymer with *trans*-(PBu₃)₂PdCl₂ in the presence of CuI catalyst at room temperature, selective cleavage of the palladium-carbon bond took place to give, exclusively, *trans,trans,trans*-ClPd(PBu₃)₂-C≡C-C≡C-Pt(PBu₃)₂-C≡C-C≡C-C-Pd(PBu₃)₂Cl (III) (eq. 9). If a mixed metal polymer has no alternating



(IIa)



(III)

regularity, depolymerization products with various numbers of platinum atoms should be produced in addition to the trinuclear complex, III. As shown in Fig. 3, GPC analysis of depolymerization products shows that the mixed metal polymer IIa gave the trinuclear complex III as the sole product, while IIb gave various oligomers. The trinuclear complex III was isolated from IIa in 75% yield by alumina column chromatography.

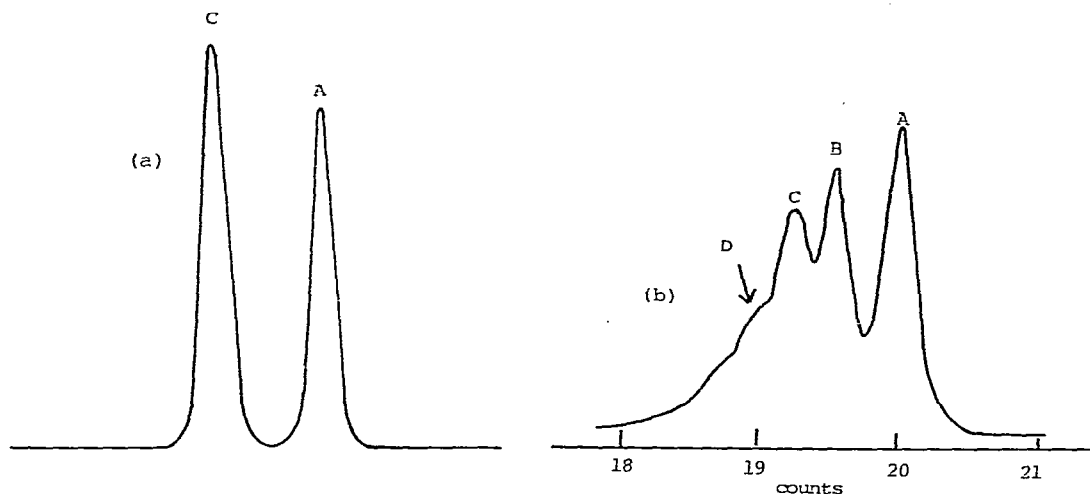


Fig. 3. Gel permeation chromatograms of depolymerization products obtained (a) from IIa, and (b) from IIb (see eq. 9). A, $(\text{Bu}_3\text{P})_2\text{PdCl}$; B, $\text{ClPd}(\text{PBu}_3)_2\text{-C}\equiv\text{C-C}\equiv\text{C-Pd}(\text{PBu}_3)_2\text{Cl}$ (V); C, $\text{ClPd}(\text{PBu}_3)_2\text{-C}\equiv\text{C-C}\equiv\text{C-Pt}(\text{PBu}_3)_2\text{-C}\equiv\text{C-C}\equiv\text{C-Pd}(\text{PBu}_3)_2\text{Cl}$ (III); D, tetranuclear complexes.

From the above data, we conclude that polymer IIa has a strictly alternating regularity of arrangement of the metals in the polymer backbone.

Experimental

All reactions were carried out under a nitrogen atmosphere.

Apparatus: ^{31}P NMR spectra were recorded on a JEOL FX 100 spectrometer, IR spectra on a Hitachi 295 spectrometer, ESCA on a Shimadzu-DuPont 650 electron spectrometer employing Mg-K_α radiation. Decomposition points were determined by using a Shimadzu Thermal Analyzer DT-30. Gel permeation chromatograms were obtained using a Shimadzu-DuPont liquid chromatograph Model 830.

Materials: Starting materials, $\text{trans}(\text{PBu}_3)_2\text{MCl}_2$ ($\text{M} = \text{Pt}, \text{Pd}$) and $\text{HC}\equiv\text{C-C}\equiv\text{CH}$ were prepared by standard procedures [7]. $\text{trans}(\text{PBu}_3)_2\text{M}(\text{C}\equiv\text{C-C}\equiv\text{CH})_2$ ($\text{M} = \text{Pt}, \text{Pd}$) was prepared from $\text{trans}(\text{PBu}_3)_2\text{MCl}_2$ and $\text{HC}\equiv\text{C-C}\equiv\text{CH}$ in the presence of CuI catalyst in HNEt_2 , $\text{trans}(\text{PBu}_3)_2\text{PdCl}(\text{C}\equiv\text{CC}_6\text{H}_5)$ from $\text{trans}(\text{PBu}_3)_2\text{PdCl}_2$ and $\text{HC}\equiv\text{CC}_6\text{H}_5$ [5,8].

$\text{-[Pt}(\text{PBu}_3)_2\text{-C}\equiv\text{C-C}\equiv\text{C-Pd}(\text{PBu}_3)_2\text{-C}\equiv\text{C-C}\equiv\text{C}]_{n/2}$ (IIa). A mixture of $\text{trans}(\text{PBu}_3)_2\text{Pt}(\text{C}\equiv\text{C-C}\equiv\text{CH})_2$ (698 mg, 1 mmol) and $\text{trans}(\text{PBu}_3)_2\text{PdCl}_2$ (582 mg, 1 mmol) in 40 ml of HNEt_2 was allowed to react in the presence of CuI (1.9 mg, 0.01 mmol) at room temperature for 20 h and then evaporated to dryness under reduced pressure. In order to remove the cuprous compound, the residue was dissolved in CH_2Cl_2 and the resulting solution filtered by alumina column chromatography. After evaporation of the filtrate, a pale yellow product was collected and purified by repeated precipitation from CH_2Cl_2 with MeOH . Finally, a benzene solution (50 ml) of the product was frozen and then freeze-dried under reduced pressure to afford a pale yellow polymer of IIa having inherent viscosity of 0.35 dL/g (in THF at 25°C). M_w 26 000 (measured by GPC [4] using a and K values of 1.7 and 6.5×10^{-9} , respectively). Yield, 1.14 g (95%).

The polymer IIb was prepared similarly from the condensation reaction between *trans*-(PBu₃)₂Pd(C≡C-C≡CH)₂ (602 mg, 1 mmol) and *trans*-(PBu₃)₂-PtCl₂ (671 mg, 1 mmol) in the presence of CuI (1.9 mg) under reflux for 6 h. A similar procedure gave the pale yellow polymer IIb in 90% yield.

$\text{-[Pd(PBu}_3)_2\text{-C}\equiv\text{C-C}\equiv\text{C}]_n\text{-}$ (VI). Following the same procedure as described for IIa, a mixture of *trans*-(PBu₃)₂Pd(C≡C-C≡CH)₂ (602 mg, 1 mmol) and *trans*-(PBu₃)₂PdCl₂ (582 mg, 1 mmol) gave the pale yellow polymer VI in 85% yield.

trans,trans,trans-ClPd(PBu₃)₂-C≡C-C≡C-Pt(PBu₃)₂-C≡C-C≡C-Pd(PBu₃)₂Cl (III). A mixture of *trans*-(PBu₃)₂Pt(C≡C-C≡CH)₂ (349 mg, 0.5 mmol) and *trans*-(PBu₃)₂PdCl₂ (873 mg, 1.5 mmol) in HNet₂ (50 ml) was allowed to react in the presence of CuI (5 mg, 0.026 mmol) at room temperature for 3 h. Evaporation of the solvent and purification of the residue by chromatography on alumina with hexane/benzene gave yellow crystals of III in 65% yield.

trans,trans,trans-ClPt(PBu₃)₂-C≡C-C≡C-Pt(PBu₃)₂-C≡C-C≡C-Pt(PBu₃)₂Cl (IV). This complex was prepared in 40% yield in a manner similar to III, using *trans*-(PBu₃)₂Pt(C≡C-C≡CH)₂ (349 mg, 0.5 mmol) and *trans*-(PBu₃)₂PtCl₂ (1.00 g, 1.5 mmol).

trans,trans,trans-ClPd(PBu₃)₂-C≡C-C≡C-Pd(PBu₃)₂Cl (V). Similarly this complex was prepared in 90% yield by the reaction of *trans*-(PBu₃)₂Pd(C≡C-C≡CH)₂ (1.00 g, 1.64 mmol) and *trans*-(PBu₃)₂PdCl₂ (2.87 g, 4.92 mmol) in the presence of CuI catalyst.

trans-ClPd(PBu₃)₂-C≡CC₆H₅ (VII). Similarly this complex was prepared in 90% yield using *trans*-(PBu₃)₂Pd(C≡CC₆H₅)₂ (71 mg, 0.1 mmol), *trans*-(PBu₃)₂-PdCl₂ (58 mg, 0.1 mmol) and CuI catalyst (2 mg).

Depolymerization of IIa. A mixture of IIa (313 mg) and *trans*-(PBu₃)₂PdCl₂ (582 mg, 1 mmol) in HNet₂ (40 ml) was allowed to react in the presence of CuI (5 mg, 0.025 mmol) at room temperature for 6 h. After evaporation of the solvent, the residue was analyzed by gel permeation chromatography (see Fig. 3a). Purification of the residue by column chromatography on alumina with hexane/benzene gave yellow crystals of III in 75% yield.

Polymer VI was also depolymerized in a manner similar to the above procedure, using VI (275 mg), *trans*-(PBu₃)₂PdCl₂ (580 mg, 1 mmol) and CuI (1.9 mg, 0.01 mol), to give V in 90% yield.

Acknowledgement

The authors wish to thank the Ministry of Education, Japan, for a Grant-in-Aid (No. 243007).

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